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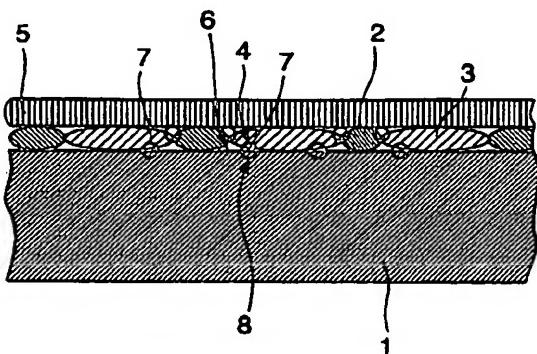
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[機密有]

(54)Title: PROTON-CONDUCTIVE ELECTRODE, PROCESS FOR PRODUCING THE SAME, AND ELECTROCHEMICAL DEVICE

(54)発明の名称: プロトン伝導性電極及びその製造方法、並びに電気化学デバイス



(57)Abstract: A proton-conductive electrode useful in fuel cells which is constituted of a mixture comprising an electron-conductive catalyst and a fullerene derivative having, incorporated onto the carbon atoms constituting the fullerene molecule, a group releasing a proton (H^+). The proton-conductive electrode is produced by applying a mixture comprising a fullerene derivative and an electron-conductive catalyst to a gas-permeable collector.

(57)要約:

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本発明は、燃料電池に用いて有用なプロトン伝導性電極であり、フラーレン分子を構成する炭素原子にプロトン (H^+) 解離性の基を導入してなるフラーレン誘導体と、電子伝導性の触媒とを含有する混合物とから構成されている。このプロトン伝導性電極は、フラーレン誘導体と電子伝導性の触媒とを含有する混合物をガス透過性集電体に塗布して製造される。

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PROTON-CONDUCTIVE ELECTRODE, PROCESS FOR PRODUCING THE SAME, AND ELECTROCHEMICAL DEVICE

Description of EP1255314

Technical Field

[0001] This invention relates to a proton (H^{+}) conducting electrode, a method for its preparation and to an electro-chemical device employing this proton conducting electrode.

Background Art

[0002] A variety of electro-chemical devices, constructed on the basis of a reaction of decomposition of a hydrogen gas, or a chemical substance containing hydrogen atoms, on an electrode to yield protons (H^{+}) and electrons, a reaction of protons and electrons to yield hydrogen, or a reaction of protons, electrons and oxygen or another substance to yield water or a further substance, such as fuel batteries or other proton-type batteries, or chemical sensors, have been proposed.

[0003] Since electrons, protons and other substances, such as hydrogen gas, oxygen gas or water, are involved in the above various reactions, the site where all of these substances meet together represents a sole site of reaction.

[0004] For example, if a catalyst exhibiting electronic conductivity is supplied in a more or less dispersed state onto the surface of a proton conductor, the contact point between the protonic conductor and electrons and in its vicinity represent a site where protons, electrons and other gaseous substances can exist together. In general, such site is termed a three-phase interface.

[0005] Fig. 1 shows a prior-art example of an electrode structure. In the electrode structure, shown in Fig. 1, a catalyst 3 exhibiting electronic conductivity is dispersed on the surface of a proton conductor 1, with the surface of the catalyst being then covered by a gas transmitting current collector 5. If only the surface of the proton conductor 1, with the catalyst 3 dispersed thereon, is used for the reaction yielding the protons (H^{+}) and electrons, a three-phase interface 7 is present in the vicinity of contact points of the proton conductor 1 and the catalyst 3. However, the site where all of electrons (e^{-}) 4, protons (H^{+}) 8 and gases 6, such as hydrogen gas or oxygen gas, meet together, is limited to a point-like area, this point-like area serving as a sole three-phase interface, with the result that the function as the electrode is not manifested satisfactorily.

[0006] Currently, for improving the function as an electrode, such a technique is used which consists in mixing proton-conducting components into an electrode material for forming a three-phase interface on the surface of the protonic conductor throughout the entire electrode formed to a certain thickness.

[0007] With this technique, electronic conducting paths are formed in a meshed pattern within the electrode by the catalyst itself or by an electrically conductive assistant material specifically mixed into the electrode material, whilst the proton conductor contained is also formed in a meshed pattern. If the other component than protons and electrons is a gas, the electrode itself is to be porous to allow the gas to be permeated throughout the electrode. If the other component is not a gas but a solid phase, the solid phase is added to the electrode. In any of these cases, the three-phase interface is to be formed over the entire electrode, as described above, to provide for as many reaction points as possible to improve the function as the electrode.

[0008] It is noted that, in the above electrode operating at a temperature lower than 100 DEG C, inclusive of the ambient temperature, a proton dissociating liquid or a proton conducting high-polymer solid electrolyte, such as Nafion, manufactured by Du Pont, de Nemur, is currently used as the protonic conductor mixed into the electrode. In particular, with the use of Nafion, the device may be solidified, and hence may find extensive application. Thus, the device tends to be used extensively as a fuel battery for

low temperature.

[0009] However, Nafion, which is a solid material, suffers a problem that, by reason of its proton conduction mechanism, its proton conduction performance is not displayed except if the Nafion itself is soaked with a sufficient amount of water. Thus, if Nafion is contained in an electrode, the device is difficult to use continuously under a dry atmosphere.

Disclosure of the Invention

[0010] In view of the above-described status of the art, it is an object of the present invention to provide a proton conducting electrode in which three-phase interface exists abundantly within the electrode and which not only is superior in its functions as electrode but exhibits only small atmosphere dependency, a method for its preparation, and an electro-chemical device.

[0011] For accomplishing the above object, the present invention provides a proton conducting electrode comprising of a mixture including a fullerene derivative and an electron conducting catalyst, wherein the fullerene derivative is composed of carbon atoms forming fullerene molecules and a proton dissociating group introduced into the carbon atoms.

[0012] In the present invention, the 'proton dissociating group' means a functional group capable of releasing protons on electrolytic dissociation, while 'dissociation of protons ($H<+>$)' means separation of protons from the functional group on electrolytic dissociation.

[0013] Since the proton conducting electrode of the present invention is comprised of the fullerene derivative having the capability of proton dissociation, and the electron conducting catalyst, the three-phase interface can be made to exist in a sufficient quantity in the electrode and hence is superior in its function in generating and propagating the protons.

[0014] Since the proton conducting electrode of the present invention uses the fullerene derivative, it exhibits only negligible atmosphere dependency such that it manifests superior proton conductivity even in a dry atmosphere. However, it may also be used in the presence of the moisture.

[0015] The proton conducting electrode according to the present invention is prepared by a method consisting in coating a mixture of a fullerene derivative, composed of carbon atoms forming fullerene molecules and a proton dissociating group introduced into the carbon atoms, on a gas transmitting current collector.

[0016] Since the proton conducting electrode according to the present invention can be produced by a step of coating the above-mentioned mixture on the gas transmitting current collector, the particle distribution density can be adjusted with relative ease. Moreover, since the mixture can be coated in multiple layers, a desired film thickness can be produced.

[0017] The electro-chemical device according to the present invention includes a first electrode, a second electrode and a proton conductor sandwiched between these first and second electrodes, wherein a proton conducting electrode comprising of a mixture of a fullerene derivative and an electron conducting catalyst, wherein the fullerene derivative is composed of carbon atoms forming fullerene molecules and a proton dissociating group introduced into the carbon atoms, forms at least the first electrode of the first and second electrodes.

[0018] In the electro-chemical device according to the present invention, in which at least the first electrode of the first and second electrodes is constructed by the proton conducting electrode, composed of the fullerene derivative and the catalyst, superior current density and output characteristics can be achieved. The present electro-chemical device is not necessarily in need of moisture, such that it manifests superior properties even under a dry atmosphere, and can be used continuously.

[0019] Other objects, features and advantages of the present invention will become more apparent from reading the embodiments of the present invention as shown in the drawings.

Brief Description of the Drawings

Fig. 1 is a schematic cross-sectional view showing a conventional electrode employing a proton conductor.

Figs.2A and 2B show molecular structures of C60 and C70, respectively.

Figs.3A and 3B show structures of fullerene polyhydroxide as typical of a fullerene derivative used in the present invention.

Figs.4A and 4B are schematic views showing examples of fullerene derivatives.

Figs.5 and 6 are schematic views showing examples of a proton conductor used in the present invention.

Fig.7 is a schematic view showing an example of a proton conductor used in the present invention.

Fig.8 schematically shows a structure of a fuel battery employing a proton conducting electrode according to the present invention.

Figs.9A and 9B show electrical equivalent circuits of a pellet used in the embodiments of the present invention.

Fig.10 is a graph showing the results of comparison of the complex impedance of the pellet.

Fig.11 is a graph showing the temperature dependency of the protonic conductivity of the pellet.

Fig.12 shows the results of power generation of a fuel battery employing a proton conducting electrode according to the present invention.

Best Mode for Carrying out the Invention

[0021] The present invention is now explained in detail with reference to its preferred embodiments.

[0022] There is no particular limitation to fullerene molecules, as a matrix into which proton dissociating groups, used in the present invention, are to be introduced, provided that they are spherically-shaped cluster molecules. However, fullerene molecules per se, as selected from C14, C20 (see Fig.2A), C70 (see Fig.2B), C76, C78, C80, C82 or C84, or mixtures of two or more of these fullerene molecules, are usually preferred.

[0023] These fullerene molecules were discovered in the mass spectrograph of a cluster beam by laser ablation of carbon in 1985 (Kroto, H.W.; Heath, J.R.; O'brien, S.C.; Curl, R.F.; Smalley, R.E. Nature 1985, 318, 162). The manufacturing method was actually established five years later. That is, in 1990, the manufacturing method by the arc discharge method of carbon electrodes was found and, since that time, fullerene attracted notice as being a carbonaceous semiconductor material.

[0024] The present inventors conducted variegated researches into the proton conductivity of derivatives of fullerene molecules, and found that fullerene polyhydroxide, obtained on introducing hydroxy groups into the constituent carbon atoms of fullerene, exhibits high protonic conductivity over a wide temperature range inclusive of an ambient temperature range, that is over a temperature range of at least 160 DEG to -40 DEG C, inclusive of the solidifying point and boiling point of water. It was also found that this protonic conductivity becomes more outstanding when a hydrogen sulfate ester group is introduced in place of the hydroxy group into the constituent carbon atoms of fullerene.

[0025] More specifically, fullerene polyhydroxide is a generic term of compounds comprised of fullerene and a plural number of hydroxy groups added thereto, as shown in Figs.3A and 3B, and is commonly named fullerol. As a matter of course, the number of hydroxy groups or the arrangement thereof in the molecular structure may be varied in a number of ways. Synthesis examples of fullerol were first reported in 1992 by Chiang et al (Chiang, L.Y.; Swirczewski, J.W.; Hsu, C.S.; Chowdhury, S.K.; Cameron, S.; Creegan, K., J. Chem. Soc., Chem. Commu. 1992, 1791). Since that time, fullerol, having hydroxy groups introduced in more than a preset amount therein, has attracted notice in particular as to its water-solubility, and has been researched mainly in the bio-related technical field.

[0026] The present inventors have formed fullerol into an aggregate, as shown schematically in Fig.4A, so that interaction will be produced between hydroxy groups of proximate fullerol molecules, indicated ˆ in the drawing, and have found, for the first time, that this aggregate exhibits high protonic conductivity, in other words, dissociation of H<+> from phenolic hydroxy groups of the fullerol

molecules, as a macroscopic mass.

[0027] The object of the present invention may also be accomplished by using a fullerene aggregate, having plural -OSO₃H groups, in addition to fullerenol, as a proton conductor. Fullerene polyhydroxide, in which OSO₃H groups take the place of OH groups, as shown in Fig.4B, that is hydrogen sulfate ester type fullerenol, was also reported by Chiang et al in 1994 (Chiang, L.Y.; Wang, L.Y.; Swirczewski, J.W.; Soled, S.; Cameron, S., J. Org. Chem. 1994, 59, 3960). It should be noted that only OSO₃H groups or a plural number of each of this group and the hydroxy group may also be contained in one molecule of the hydrogen sulfate ester type fullerenol.

[0028] As for the protonic conductivity, demonstrated on aggregating a large quantity of the above-mentioned fullerene derivative into a bulk material, the protons derived from the large number of hydroxy groups or OSO₃H groups, inherently contained in the fullerene molecules, directly take part in migration, so that there is no necessity of capturing hydrogen or protons, derived from e.g., water vapor molecules, from atmosphere, or of replenishing water from outside, in particular, absorbing water from outside, there being no constraint imposed on the atmosphere to be in use. On the other hand, fullerene, forming the basis of these derivative molecules, exhibit electrophilic properties, which are felt as significantly contributing to the promotion of ionization of hydrogen ions not only in highly acidic OSO₃H groups but also in hydroxy groups. This accounts for excellent protonic conductivity of the proton conductor of the present invention.

[0029] Moreover, since a larger amount of hydroxyl and OSO₃H groups can be introduced into one fullerene molecule, the number density of protons taking part in conduction per unit volume of the conductor is increased appreciably. This also accounts for an effective conductivity displayed by the proton conductor of the present invention.

[0030] The major portion of the proton conductor of the present invention is constituted by carbon atoms of fullerene, so that it is light in weight, unsusceptible to deterioration and is free of pollutants. The manufacturing cost of fullerene is also being lowered precipitously. Thus, in the light of resources, environment and economical merits, fullerene is felt to be a carbonaceous material closer to an ideal material than any other comparable materials.

[0031] Our investigations have revealed that there is no necessity of limiting the proton dissociating group to the aforementioned hydroxyl groups or OSO₃H group.

[0032] Thus, it is sufficient if this dissociating group is represented by -XH, with X being an atom or group of atoms having divalent bonds. It is also sufficient if this group is represented by -OH or -YOH, with Y being an arbitrary atom or group of atoms having divalent bonds.

[0033] Specifically, the proton dissociating group may be any one of -COOH, -SO₃H or -PO(OH)₂, in addition to -OH and -OSO₃H.

[0034] For synthesizing a fullerene derivative, used in a proton conducting electrode according to the present invention, it is sufficient if any suitable proton dissociating group is introduced into constituent carbon atoms of fullerene molecules, by applying known processing techniques, such as acid processing or hydrolysis, in any suitable combination, to the powders of fullerene molecules.

[0035] According to the present invention, the mixture containing fullerene derivatives and electron conducting catalysts are desirably porous, with the porosity being preferably in a range of 1 to 90%. This enables the gas to be diffused to the entire electrode so as to form a three-phase interface in the entire electrode to increase the number of reaction points to improve the function of the electrode in generating and propagating protons.

[0036] The mixing ration by weight of the fullerene derivatives and the catalyst in the mixture containing fullerene derivatives and the electron conducting catalyst is preferably 1:100 to 100:1.

[0037] Moreover, the mixture is preferably formed in a layered form on a gas transmitting current collector, such as carbon paper. The mixture may be present as a sole layer or in a multi-layer structure.

[0038] The proton conducting electrode according to the present invention is comprised of a gas transmitting current collector on which a mixture comprised of the fullerene derivatives and the electron

conducting catalyst is formed as a sole layer or in a multi-layer structure, as described above, as shown in Figs.5 and 6.

[0039] In the proton conducting electrode, shown in Fig.5, a porous mixture, containing the fullerol molecules 2 as a fullerol derivative and the electron conducting catalyst 3, is diffusively coated on the surface of the proton conductor 1, with the surface of the porous mixture then being coated with the gas transmitting current collector 5.

[0040] On the other hand, the proton conducting electrode, shown in Fig. 6, is obtained on coating a porous mixture of fullerol molecules 2 and an electron conducting catalyst 3 in multiple layers.

[0041] The proton conducting electrode of the present invention, constructed as shown in Figs.5 and 6, uses a porous mixture containing fullerol molecules 2 and the electron conducting catalyst 3, so that the gas can be permeated throughout the entire electrode. Moreover, since the fullerol molecules 2 as a fullerene derivative having a proton dissociating capability and the electron conducting catalyst 3 are formed throughout the inside of the electrode, there is produced a three-phase interface 7 not only in the vicinity of a contact point between the proton conductor 1 and the catalyst 3, but also in the vicinity of a contact point between the catalyst 3 and the fullerol molecules 2. This three-phase interface 7 is a site where the electrons (e^{-}) 4, protons (H^{+}) electrons and the gases 6, such as hydrogen or oxygen gases all meet simultaneously.

[0042] Since the proton conducting electrode of the present invention is capable of producing the three-phase interface 7 not only in the vicinity of the contact point between the proton conductor 1 and the catalyst 3, but also in the vicinity of the contact point between the catalyst 3 and the fullerol molecules 2, the function of the electrode in generating and propagating protons can be improved. Additionally, since the proton conducting electrode contains the fullerene derivative having the proton dissociating capability, the electrode can be used continuously even in a dry atmosphere.

[0043] The catalyst forming a porous mixture used in the proton conducting electrode according to the present invention is preferably formed of the porous material carrying electron conducting atoms. In this case, the amount of electron conducting atoms, carried by the porous material, is preferably 10 to 50 wt%.

[0044] The atoms exhibiting electron conductivity (catalytic metal) may be platinum, ruthenium, vanadium, tungsten or mixtures thereof, whilst the porous material may be carbon powders, porous Ni-Cr sintered material, Al₂O₃ sintered material, or a porous plate of Li-Cr alloy. Of these, the combination of platinum and carbon powders is desirable.

[0045] Preferably, electron conducting atoms are present in an amount of 0.1 to 10 mg/cm² between the proton conductor 1 and the gas transmitting current collector 5.

[0046] The proton conducting electrode according to the present invention can be used with advantage in a variety of electro-chemical devices. That is, in a basic structure including first and second electrodes and a proton conductor sandwiched between these electrodes, at least the first one of the first and second electrodes may be the proton conducting electrode embodying the present invention.

[0047] The proton conducting electrode embodying the present invention may be used for e.g., an electro-chemical device in which at least one of the first and second electrodes is a gas electrode.

[0048] The fuel battery employing the proton conducting electrode of the present invention is hereinafter explained.

[0049] The mechanism of proton conduction of the present fuel battery is as shown in the schematic view of Fig.7. A proton conduction unit 9 is sandwiched between a first electrode 10, for example, a hydrogen electrode, and a second electrode 11, for example, an oxygen electrode, and dissociated protons (H^{+}) are migrated from the first electrode 10 towards the second electrode 11, as indicated by arrow in the drawing.

[0050] Fig.8 shows an exemplary fuel battery employing the proton conducting electrode according to the present invention. As shown in Fig.8, this fuel battery includes a negative electrode 10, having a terminal 15 at one end, and which uses the proton conducting electrode according to the present invention, and a

positive electrode 11, having a terminal 16 at one end, and which also uses the proton conducting electrode. The negative electrode 10 constitutes a fuel battery or a hydrogen cell, whereas the positive electrode 11 constitutes an oxygen electrode. Meanwhile, it is not mandatory to use the proton conducting electrode of the present invention as the positive electrode 11. The negative electrode 10 and the positive electrode 11 are arranged parallel to and facing each other, and the proton conduction unit 9 is sandwiched between the negative electrode 10 and the positive electrode 11, as shown in Fig.8.

[0051] In use of the fuel battery, constructed as shown in Fig.8, hydrogen acting as a fuel 19 is sent via an inlet 17 at the negative electrode 10 so as to be discharged at an exit port 18 which is not mandatory. A fuel (H₂) 19, supplied through inlet 17, yields protons as it traverses a flow channel 20, these protons migrating along with the protons generated in the negative electrode 2 and protons generated in the proton conduction unit 9 towards the positive electrode 11 where the protons are reacted with oxygen (air) 24 supplied from the inlet 21 to the flow channel 22 and which is thence sent towards an exhaust port 23, thereby producing the desired electromotive force.

[0052] With the fuel battery of the present invention, employing the proton conducting electrode of the present invention, and constructed as shown in Fig.8, protons are dissociated in the negative electrode 10 and, as the protons are dissociated in the proton conduction unit 9, the protons supplied from the negative electrode 10 are migrated towards the positive electrode 11, thus improving proton conductivity. Consequently, with the fuel battery of the present invention, no humidifying device etc is needed, so that the system is simplified and reduced in weight, while the function of the electrode, such as electrical density or output characteristics, may be improved.

[0053] In the electrochemical device, such as fuel battery, embodying the present invention, there is no particular limitation to the proton conductor sandwiched between the proton conducting electrodes, such that any suitable material exhibiting proton conductivity, such as fullerene hydroxide, hydrogen sulfate ester type fullerenol or Nafion, for example, may be used.

[0054] An example of the present invention is now explained in detail.

Example

<Synthesis of fullerene polyhydroxide>

[0055] This synthesis was carried out using a reference material (Chiang, L.Y.; Wang, L.Y.; Swirczewski, J.W.; Soled, S.; Cameron, S., J. Org. Chem.. 1994; 59, 3960). 2 g of powders of C₆₀/C₇₀ fullerene mixture, containing approximately 15% of C₇₀, were charged into 30 ml of fuming sulfuric acid and stirred for three days in a nitrogen atmosphere as the temperature was maintained at 60 DEG C. The resulting reaction mass was charged gradually into anhydrous diethyl ether cooled in a glacial bath. The resulting precipitates were fractionated on centrifugation, washed thrice with diethyl ether and twice with a 2:1 liquid mixture of diethyl ether and acetonitrile and dried under reduced pressure at 40 DEG C. The dried product was charged into 60 ml of ion exchanged water and stirred for ten hours under bubbling with nitrogen at 85 DEG C. The reaction product was freed on centrifugation from precipitates which were washed several times with pure water, repeatedly centrifuged and dried under reduced pressure at 40 DEG C. The resulting brownish powders were subjected to FT-IR measurement. It was found by this measurement that the IR spectrum of the brownish powders approximately coincided with that of C₆₀(OH)₁₂, thus indicating that the powders were fullerene polyhydroxide powders as a target material. The above reaction can be represented for C₆₀ as follows:

EMI17.1

<Preparation of flocculated pellets of fullerene polyhydroxide>

[0056] 90 mg of powders of fullerene polyhydroxide were taken and pressed in one direction into circular pellets 15 mm in diameter. The pressing pressure at this time was approximately 5 ton/cm². It was

found that the powders of fullerene polyhydroxide, while containing no binder resin or the like, were superior in moldability and could be formed into a pellet extremely readily. This pellet, about 300 μm in thickness, is termed a flocculated pellet of fullerene polyhydroxide.

<Synthesis of fullerene polyhydroxide hydrogen sulfate ester (full ester)>

[0057] This synthesis was carried out using the above-mentioned reference material. 1 g of powders of fullerene polyhydroxide, was charged into 60 ml of fuming sulfuric acid and stirred for three days in a nitrogen atmosphere at ambient temperature. The resulting reaction mass was charged gradually into anhydrous diethyl ether cooled in a glacial bath. The resulting precipitates were fractionated on centrifugation, washed thrice with diethyl ether and twice with a 2:1 liquid mixture of diethyl ether and acetonitrile and dried under reduced pressure at 40 DEG C. The resulting brownish powders were subjected to FT-IR measurement. It was found by this measurement that the IR spectrum of the brownish powders approximately coincided with that of a compound all hydroxy groups of which are turned into a hydrogen sulfate ester, as indicated in the above reference material, thus indicating that the powders were fullerene polyhydroxide hydrogen sulfate ester as a target material.

[0058] The above reaction can be represented for C₆₀(OH)₃ as follows (hereinafter the same):
EMI18.1

<Preparation of flocculated pellets of fullerene polyhydroxide hydrogen sulfate ester>

[0059] 70 mg of powders of fullerene polyhydroxide hydrogen sulfate ester were taken and pressed in one direction into circular pellets 15 mm in diameter. The pressing pressure at this time was approximately 5 ton/cm². It was found that the powders, containing no binder resin or the like, were superior in moldability and could be pelletized extremely readily. This pellet, about 300 μm in thickness, is termed a flocculated pellet of fullerene polyhydroxide hydrogen sulfate ester.

<Preparation of flocculated fullerene pellet of Comparative Example>

[0060] For comparison, 90 mg of fullerene, used as a starting material for synthesis in the previous Example, were taken and pressed in one direction into circular pellets 16 mm in diameter. The pressing pressure at this time was approximately 5 ton/cm². It was found that the powders, containing no binder resin or the like, were superior in moldability and could be pelletized extremely readily. This pellet, about 300 μm in thickness, is termed a pellet of the Comparative Example.

Measurement of proton conductivity of Example (flocculated pellet of fullerene polyhydroxide hydrogen sulfate ester) and pellet of Comparative Example

[0061] For measuring the conductivity of the pellets of the Example and the Comparative Example, each of the pellets was sandwiched between a pair of aluminum plates, each being 15 mm in diameter as is the pellet. An AC voltage of an amplitude of 0.1 V was applied to each assembly, with a frequency ranging from 7 MHz to 0.01 Hz, to measure the complex impedance at each frequency. The measurement was conducted in a dry atmosphere.

[0062] In measuring the impedance, the proton conduction unit 9 of the proton conductor of the above-described embodiment, comprised of the pellet, electrically forms an equivalent circuit, shown in Fig.9A, and forms capacitances 14a, 14b across the first and second electrodes 10, 11 and the proton conduction unit 9 represented by a parallel connection of a resistance 4 and a capacitance 5. Meanwhile, a capacitance 13 represents the delay effect on proton migration (phase delay for a high frequency), while a resistance 12 represents a parameter of proton mobility.

[0063] The complex impedance Z is represented by $Z = \text{Re}(Z) + i\cdot\text{Im}(Z)$. The frequency dependency of the proton conduction unit, represented by the above-described equivalent circuit, was checked.

[0064] Fig.9B shows an equivalent circuit in case of using the ordinary fullerene molecules not having proton dissociating properties, as in the above-described Comparative Example. In Fig.9B, 9a denotes a fullerene unit.

[0065] Fig.10 shows the results of impedance measurement for the pellets in the Example and in the Comparative Example.

[0066] It may be seen from Fig.10 that the frequency response of the complex impedance is approximately similar to the response of the capacitor per se, as shown in Fig.10B, while the conduction behavior of charged particles, such as electrons or ions of the flocculated mass of the fullerene itself, was not noticed. Conversely, in the Example, an extremely fine semi-circular arc, though somewhat flat, may be observed in a high frequency portion, as shown in Fig.10A. This indicates that there exists some conduction behavior of charged particles within the pellet. Additionally, there may be noticed acute rise of the imaginary portion of the impedance in the low frequency region. This indicates that blocking of charged particles with the aluminum electrode occurs as the DC voltage is approached. Since the charged particles on the side aluminum electrode are naturally electrons, it may be seen that the charged particles within the pellet are the particles other than electrons or holes, that is ions. Judging from the structure of fullerol used, the charged particles must be no other than protons.

[0067] The conductivity of the charged particles can be found from the X-axis intercept of the arc seen towards the side high frequency side. In the pellet of the Example, it may be calculated to be approximately 5×10^{-6} S/cm. It could be found that the flocculated mass of the sort of fullerene derivative allows proton conduction at ambient temperature in a dry atmosphere.

[0068] Using the pellet of the Example (flocculated pellet of fullerene polyhydroxide hydrogen sulfate ester), the above-mentioned measurement of the complex impedance was conducted in a temperature range from 160 DEG C to -40 DEG C, to check for temperature dependency of the conductivity as found from the arc on the side high frequency. The results are shown as an Arrhenius plot in Fig.11, from which it may be seen that the conductivity is changed linearly in a temperature range from 160 DEG C to -40 DEG C. In short, this figure shows that the sole ion conduction mechanism can proceed in the above temperature range. That is, the flocculated mass of the fullerene derivative used in the present invention allows for proton conduction in a broad temperature range inclusive of the ambient temperature, in particular, even at an elevated temperature of 160 DEG C or a low temperature of -40 DEG C.

Preparation of fuel batteries of Example and Comparative Example and power generation test

[0069] Powders of carbon carrying 20 wt% of platinum (mean particle size: 50 nm) and powders of fullerene polyhydroxide hydrogen sulfate ester, obtained as described above, were mixed together at a weight ratio of 1:2 and mixed in a solution of tetrahydrofuran (THF). The resulting mixture was coated on a carbon paper to a platinum carrying amount of 1 mg/cm² to form a fullerol containing electrode of the present invention to a thickness of 50 μm.

[0070] Two fullerol containing electrodes of the present invention were prepared to form a fuel battery device comprised of these electrodes placed on both sides of a thin film of a flocculated mass of the powders of fullerene polyhydroxide (thickness: 25 μm) as a proton conductor. This fuel battery device was built in the fuel battery cell shown in Fig.8. The one side (negative electrode side) and the other side (positive electrode side) of the fuel battery device shown in Fig.8 were opened to a dry hydrogen gas and to a dry oxygen gas, respectively, to carry out a power generation test at ambient temperature.

[0071] By way of a Comparative Example, carbon powders (mean particle size: 50 nm) carrying 20 wt% of platinum were coated on a carbon paper, using a Nafion solution, to a platinum carrying amount of 1 mg/cm² and the Nafion quantity of 2 mg/cm², to prepare a Nafion mixture electrode.

[0072] Two electrodes of the Nafion mixture were prepared and placed on either sides of a thin film composed of powders of fullerene polyhydroxide (thickness: 25 μm) to prepare a fuel battery device, which then was built into a fuel battery cell shown in Fig.8. The one side (negative electrode side) and the

other side (positive electrode side) of the fuel battery device shown in Fig.8 were opened to a dry hydrogen gas and to a dry oxygen gas, respectively, to carry out a power generation test at ambient temperature.

[0073] The results of each power generation test are shown in Fig. 12.

[0074] These results indicate that, while the open voltage is approximately 1.2 V for both the Example and the Comparative Example, the Example employing the electrode of the fullerol mixture shows characteristics shown at A in Fig.12. That is, the Example is improved in current density and superior in output characteristics as compared to the Comparative Example of the electrode of the Nafion mixture shown at B in Fig.12.

Industrial Applicability

[0075] Since the proton conducting electrode of the present invention is a mixture of a fullerene derivative and an electron conducting catalyst, in which the fullerene derivative is composed of carbon atoms forming fullerene molecules and proton dissociating groups introduced therein, a three-phase interface can be present in a sufficient quantity in the electrode, so that the electrode is superior in its function in generating and propagating protons.

[0076] Moreover, since the proton conducting electrode uses a fullerene derivative, it is low in atmosphere dependency and can be used continuously even in a dry atmosphere, so that it is able to demonstrate superior proton conductivity desired the electro-chemical device.

[0077] Since no atmosphere constraint is placed on the electro-chemical device, employing the proton conducting electrode according to the present invention, the system can be reduced in size and simplified in structure, while it is possible to develop optimum current density and output characteristics.

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**PROTON-CONDUCTIVE ELECTRODE, PROCESS FOR PRODUCING THE SAME,
AND ELECTROCHEMICAL DEVICE**

Claims of EP1255314

1. A proton conducting electrode comprising of a mixture including a fullerene derivative and an electron conducting catalyst, wherein the fullerene derivative is composed of carbon atoms forming fullerene molecules and a proton dissociating group introduced into said carbon atoms.
2. The proton conducting electrode according to claim 1 wherein said proton dissociating group is -XH, where X is an atom having a divalent bond, and H is a hydrogen atom.
3. The proton conducting electrode according to claim 1 wherein said proton dissociating group is -OH or -YOH, where Y is an atom or a group of atoms having a divalent bond.
4. The proton conducting electrode according to claim 3 wherein said proton dissociating group is selected from the group consisting of -OH, -OSO₃H, -COOH, -SO₃H and -PO(OH)₃.
5. The proton conducting electrode according to claim 1 wherein said mixture is porous.
6. The proton conducting electrode according to claim 1 wherein said mixture is of a single-layer or multi-layer structure.
7. The proton conducting electrode according to claim 1 wherein said mixture is formed as a layer on a gas transmitting current collector.
8. The proton conducting electrode according to claim 1 wherein said catalyst is a porous material carrying atoms exhibiting electron conductivity.
9. The proton conducting electrode according to claim 1 wherein the mixing ratio by weight of said fullerene derivative and the catalyst in said mixture is 1:100 to 100:1.
10. The proton conducting electrode according to claim 1 wherein said mixture has a porosity of 1 to 90%.
11. The proton conducting electrode according to claim 7 wherein the gas transmitting current collector is carbon paper.
12. The proton conducting electrode according to claim 8 wherein the electron conducting atom is platinum and said porous material is carbon powders.
13. The proton conducting electrode according to claim 8 wherein the amount of the electron conducting atoms carried by said porous material is 1 to 50 wt%.
14. The proton conducting electrode according to claim 8 wherein the electron conducting atoms are present on said gas transmitting current collector in an amount of 0.1 to 10 mg/cm<2>.
15. The proton conducting electrode according to claim 1 wherein said fullerene molecules are molecules of a spherically-shaped carbon cluster C_m, where m = 36, 60, 70, 76, 78, 82, 84 etc.
16. A method for the preparation of a proton conducting electrode comprising:
coating a mixture of a fullerene derivative, composed of carbon atoms forming fullerene molecules and a proton dissociating group introduced into said carbon atoms, on a gas transmitting current collector, and an electron conducting catalyst.
17. The proton conducting electrode according to claim 16 wherein said proton dissociating group is -XH, where X is an atom having a divalent bond, and H is a hydrogen atom.

18. The proton conducting electrode according to claim 16 wherein said proton dissociating group is -OH or -YOH, where Y is an atom or a group of atoms having a divalent bond.
19. The proton conducting electrode according to claim 16 wherein said proton dissociating group is selected from the group consisting of -OH, -OSO₃H, -COOH, -SO₃H and -PO(OH)₃.
20. The proton conducting electrode according to claim 16 wherein said mixture is porous.
21. The proton conducting electrode according to claim 16 wherein said mixture is coated as a single layer or as a multiple layer.
22. The proton conducting electrode according to claim 16 wherein said catalyst is a porous material carrying atoms exhibiting electron conductivity.
23. The proton conducting electrode according to claim 16 wherein the mixing ratio by weight of said fullerene derivative and the catalyst in said mixture is 1:100 to 100:1.
24. The proton conducting electrode according to claim 16 wherein said mixture has a porosity of 1 to 90%.
25. The proton conducting electrode according to claim 16 wherein the gas transmitting current collector is carbon paper.
26. The proton conducting electrode according to claim 22 wherein the electron conducting atom is platinum and said porous material is carbon powders.
27. The proton conducting electrode according to claim 22 wherein the amount of the electron conducting atoms carried by said porous material is 1 to 50 wt%.
28. The proton conducting electrode according to claim 22 wherein the electron conducting atoms are present on said gas transmitting current collector in an amount of 0.1 to 10 mg/cm².
29. The proton conducting electrode according to claim 16 wherein said fullerene molecules are molecules of a spherically-shaped carbon cluster C_m, where m = 36, 60, 70, 76, 78, 82, 84 etc.
30. An electro-chemical device comprising a first electrode, a second electrode and a proton conductor sandwiched between these first and second electrodes, wherein a proton conducting electrode, comprised of a mixture including a fullerene derivative and an electron conducting catalyst, wherein the fullerene derivative is composed of carbon atoms forming fullerene molecules and a proton dissociating group introduced into said carbon atoms, forms at least said first electrode of said first and second electrodes.
31. The electro-chemical device according to claim 30 wherein said proton dissociating group is -XH, where X is an atom having a divalent bond, and H is a hydrogen atom.
32. The electro-chemical device according to claim 30 wherein said proton dissociating group is -OH or -YOH, where Y is an atom or a group of atoms having a divalent bond.
33. The electro-chemical device according to claim 30 wherein said proton dissociating group is selected from the group consisting of -OH, -OSO₃H, -COOH, -SO₃H and -PO(OH)₃.
34. The electro-chemical device according to claim 30 wherein said mixture is porous.
35. The electro-chemical device according to claim 1 wherein said mixture is coated as a single layer or as a multiple layer.
36. The electro-chemical device according to claim 30 wherein said mixture is formed as layers on a gas-transmitting current collector.
37. The electro-chemical device according to claim 30 wherein said catalyst is a porous material carrying atoms exhibiting electron conductivity.

38. The electro-chemical device according to claim 30 wherein the mixing ratio by weight of said fullerene derivative and the catalyst in said mixture is 1:100 to 100:1.
39. The electro-chemical device according to claim 30 wherein said mixture has a porosity of 1 to 90%.
40. The electro-chemical device according to claim 30 wherein the gas transmitting current collector is carbon paper.
41. The electro-chemical device according to claim 37 wherein the electron conducting atom is platinum and said porous material is carbon powders.
42. The electro-chemical device according to claim 37 wherein the amount of the electron conducting atoms carried by said porous material is 1 to 50 wt%.
43. The electro-chemical device according to claim 37 wherein the electron conducting atoms are present on said gas transmitting current collector in an amount of 0.1 to 10 mg/cm².
44. The electro-chemical device according to claim 30 wherein said fullerene molecules are molecules of a spherically-shaped carbon cluster C_m, where m = 36, 60, 70, 76, 78, 82, 84 etc.
45. The electro-chemical device according to claim 30 wherein at least one of said first and second electrodes is a gas electrode.
46. The electro-chemical device according to claim 45 wherein the device is constructed as a fuel battery.

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